

THE BIOGEOCHEMISTRY OF CALCRETE FORMING PROCESSES

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INTRODUCTION

Samples of calcrete and calcareous sands from the Barns gold anomaly (ca. 25 km NW of Wudinna, South Australia) were investigated to determine the relationship of gold and other trace elements with the major element variation. The strong correlation of gold with calcium and magnesium carbonates (see McEntegart & Schmidt Mumm, this volume) in the analysed samples suggest a fundamental relationship between the carbonate precipitation and gold fixation therein. Thus to understand the gold accumulation primarily means to understand the carbonate precipitating process.

The controlling parameters of carbonate formation in the regolith are the pH, the f_{O_2} , the partial pressure of P_{CO_2} , the pressure, the temperature and the concentration of the respective cations (mostly Ca^{2+} and Mg^{2+}). The variation of these parameters is assumed to be related to interdependent influences of: (i) the primary composition of the regolith host material; (ii) climatic changes, such as temperature, rainfall, evaporation; (iii) hydraulic processes within the regolith, such as moisture content, evapo-transpiration and groundwater flow; and, (iv) the impact of biological activity on pH and P_{CO_2} .

In this project we have investigated the chemical composition and variation within regolith depth profiles from the extensive sand dune systems on the Barns gold anomaly. We have also carried out "real time" measurements of relative pH and conductivity along these profiles, and biogeochemical experiments to assess the possibility of microbially mediated NH_3 -production from the breakdown of urea through the urease enzyme in these sand dunes.

BARNS AND THE SAND DUNES

The gold anomaly on the Barns property was identified by Adelaide Resources Ltd. during a regional geochemical exploration program using calcrete as a sampling medium for its demonstrated (Anand *et al.* 1997) potential to accumulate gold in low concentrations. This property allows the use of "gold in calcrete" analysis in exploration to determine gold anomalies down to a level of ca. 2.5 ppb Au, which in some cases indicate gold mineralisation in the underlying bedrock.

The Barns gold anomaly is developed in the extensive aeolian sand covers of the northern Eyre Peninsula which almost completely blanket the underlying rocks. Geochemical analyses of aeolian sand dune material were carried out to determine the compositional range as shown in Table 1.

Table 1: Compositional variation of major elements in the Barns sand dunes in wt. % oxide.

	SiO ₂	Al ₂ O ₃	Fe ₂ O _{3T}	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃	LOI
average	97.04	0.87	0.27	0.01	0.14	0.83	0.06	0.10	0.06	0.00	0.02	1.15
max.	98.80	1.01	0.31	0.01	0.21	1.80	0.09	0.12	0.07	0.01	0.03	1.97
min.	95.47	0.73	0.23	0.01	0.08	0.04	0.03	0.09	0.06	0.00	0.01	0.43

Extensive sampling was carried out on the Barns property to characterise the gold anomaly with respect to the relationship of the gold in calcrete and various other major and trace elements. Sampling was conducted using a percussion core sampler to obtain undisturbed 2 to 3 m depth profiles of material from a pronounced sand dune. Most of the sand dune consists of about 96% SiO₂ in the form of quartz sand with little compositional variation (see Table 1). Lower SiO₂ contents generally relate to elevated carbonate and in some cases clay mineral contents. Carbonate is present finely dispersed in calcareous sand or in some cases as consolidated nodular calcrete.

TRACE AND MAJOR ELEMENTS IN CALCRETE

The aeolian sand dunes on the Barns property consist largely of SiO₂ (Table 1), but this systematically changes with depth where the concentration of other major components such as Al, Ca, Mg and K increases, along with a general increase in trace element content. This suggests a more complex mineralogy in the core of the sand dunes than at their surface. One of the most intriguing patterns of gold in the sand dune material is its consistent correlation with the calcium content (Figure 1), which in turn can be shown to represent the

calcium carbonate in the samples. A similarly consistent correlation exists for the magnesium content (see also Schmidt Mumm & McEntegart, this volume). Figures 2 and 3 show the typical variation of some of the major and trace elements to depth. The investigations of the calcrete-gold association strongly suggest a common process of formation and enrichment of calcite and gold in certain parts of the regolith.

Figure 2 shows an example of the correlation of gold with the major elements in a depth profile of a sand dune. Gold content correlates well with Ca but to some extent also with Mg, K and Na. Correlation with Mg in particular may be better in some cases than in the presented example. The clearest relationship of major and trace elements follows common substitutional patterns such as Ca-Sr, K-Rb and Ca-Ba. Ag, Cu and As, which are common pathfinders of gold in weathering profiles and fresh rock, do not show any systematic variation with gold or any of the major elements. Covariance of gold exists with V and U in some instances and sometimes with Ni (Figure 3)

VARIATION OF pH AND CONDUCTIVITY IN THE SAND DUNE PROFILES

As outlined above, pH and cation concentration are important parameters of carbonate precipitation. In order to determine pH and concentration of dissolved ions the relative pH and conductivity were measured immediately after taking samples in the field. Samples were immersed in deionised water at a weight-to-volume ratio of 1:5 and measurements were conducted with portable pH and conductivity meters, calibrated to standard solutions. The results show that in the given profile the pH is at about 8.2 to 8.4 to a depth of about 2 m from where it sharply increases to values of 9.2 and above (Figure 4).

Relative conductivity is low (<50 mS) in the first 2 m. Below this it gradually increases to 170 mS at 2.5 m and then increases sharply to 1080 mS at the bottom of the hole at 3 m depth. Although the data does not represent absolute values, as measurements were carried out on

diluted extracts, they clearly demonstrate that the chemical environment at depth is one of alkaline solution with high concentration of ions, which can be considered favourable for the precipitation of carbonates.

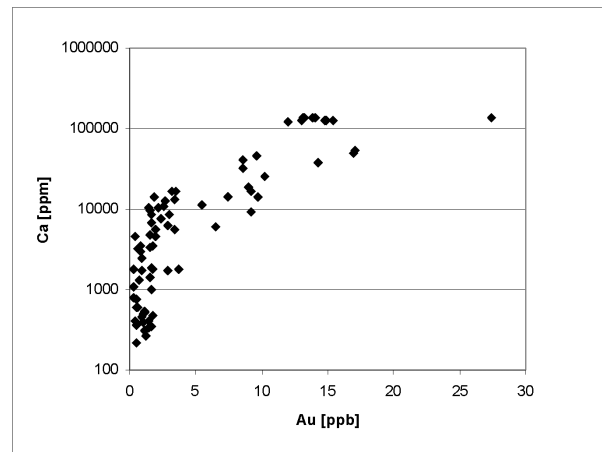


Figure 1: Gold-calcium correlation in the samples from the Barns "gold in calcrete" anomaly. The mineralogical composition of the sand dune material is described in McEntegart & Schmidt Mumm (this volume).

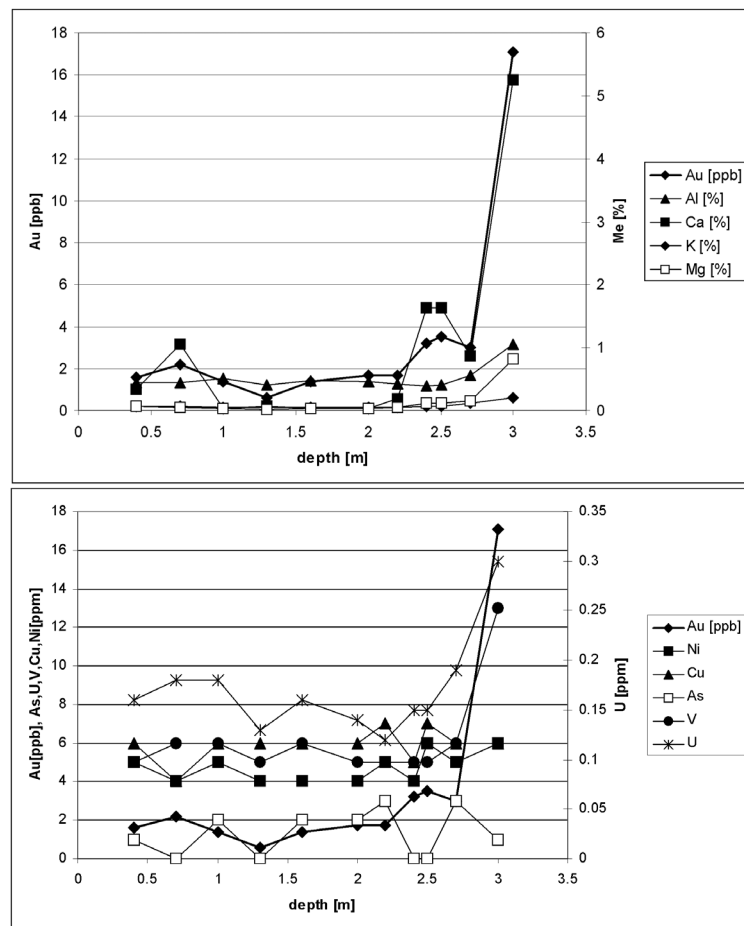


Figure 2 (top): Concentration (ppm) of Al, Ca, Mg, K and Au (ppb) in the sand dune depth profile.

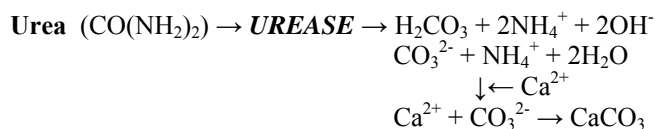
Figure 3 (bottom): Concentration (ppm) of Ni, Cu, As, V, U and Au (ppb) in the sand dune depth profile.

THE INFLUENCE OF BIOACTIVITY

Biologically induced or biogenic calcite precipitation has been described for a number of environments like aridsols (Monger *et al.* 1991). Calcified organic filaments in calcretes in South Australia and in petrocalcic horizons in France have been described by Phillips *et al.* (1987) and Amit & Harrison (1995), respectively.

One microbial process, which has been demonstrated to induce calcite precipitation is the metabolic breakdown of urea ($\text{CO}(\text{NH}_2)_2$) to CO_2 and NH_3 by activation of the urease enzyme. Biologically mediated calcite precipitation related to the activity of the urease enzyme-producing *Bacillus Pasteurii* by Stocks-Fischer *et al.* (1999) in saline soils and has been experimentally reproduced by Parraga *et al.* (2004). Bachmeier *et al.* (1999) further quantified the role of urease activity in microbiologically induced calcite precipitation through experimental work.

Urea is a product formed in soils during the decomposition of amino acids and other organic nitrogen compounds. Hydration of CO_2 leads to H_2CO_3 which, in the mildly alkaline environment produced by the reaction of $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$, dissociates readily. If Ca^{2+} ions are available, calcium carbonate is precipitated:



In this process the pH of the reaction environment is raised through the release of ammonia into regions favourable for CO_3^{2-} speciation in aqueous solution and thus calcite precipitation. In media with bacterial isolates this process has been shown to mediate calcite formation (Stocks-Fischer *et al.* 1999, Bachmeier *et al.* 1999).

SAMPLING AND ANALYTICAL PROCEDURES

In order to demonstrate the activity of this reaction in calcrite forming processes an experimental setup was designed to demonstrate the urease activity in Au-anomalous calcrite bearing materials. These investigations were carried out on samples of dune sand from the Barns prospect. The experiments shall be briefly summarised here.

1. Great care was taken to avoid contamination for the sampling. All instruments used were repeatedly washed with deionised water and then ethanol, or were flame sterilised before use. Samples, once obtained, were sealed and transported refrigerated to the laboratory in Adelaide.
2. Surface samples were taken with a small shovel, samples from depth were taken using a percussion soil corer lined with sterilised PVC pipes. Further samples were taken from a nearby wheat field and from the root zone of a spinifex bush.
3. Small (1g) samples were aseptically extracted from the PVC pipes by means of drilling holes into the pipes and transferring material into test tubes. Sampling depth intervals were at 0, 10, 39, 64, 90, 115, 146, 163, 184, 210, 230 cm. Five different sample sets were amended with sterile urea solution to a final concentration of 5 mM and 10 mM and incubated for 0, 30 and 90 min, and 24 h at 25°C:
 1. 5 mM urea, stopped immediately (control);
 2. 5 mM urea 30 min incubation;
 3. 5 mM urea 90 min incubation;
 4. 10 mM urea 24 h incubation;
 5. 10 mM urea 90 min incubation.

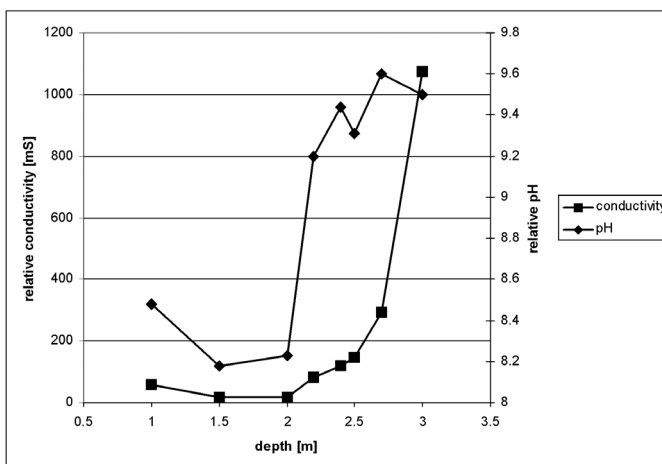


Figure 4: Relative conductivity and pH measured in the sand dune profile.

RESULTS

All surface samples showed positive for urease activity through production of NH_4^+ even after only brief incubation (Figure 5) and massively so after 24 h of incubation. Samples from the depth profile were not as readily reactive to the urease impregnation. Incubation times of 30 and 90 min produced NH_4 only in the sample closest to the surface (Figure 6).

However, all samples analysed positive for NH_4 after 24 h of incubation. The overall variation of NH_4 content was from 0.14 mg l^{-1} to 18 mg l^{-1} . Already, at a depth of only 30 cm and the NH_4 production is less than 1 mg l^{-1} and shows no correlation with major or trace element concentration, pH or conductivity.

It was thus demonstrated that the urease-enzyme induced breakdown of urea occurs in the auriferous calcrete bearing sands at the Barns calcrete-gold anomaly. This is direct indication for an at least partial microbially mediated calcite precipitation and calcite formation.

CONCLUSIONS

The correlation of gold and Ca in calcrete is a useful tool

for gold exploration. However, the process of gold accumulation in the calcrete-forming environment is only poorly understood. Microbially induced formation of carbonate through the urease enzymatic breakdown of urea is a demonstrated process for a range of soil carbonate forming environments. This process has been experimentally demonstrated for calcretes from the Barns calcrete-gold anomaly.

The relatively even production of NH_4 throughout the depth profile below 30 cm suggests that the process is largely independent of the chemical composition of the host environment. As calcium and carbonate content have been shown to strongly increase at depth alongside changes in pH and conductivity, we suggest the following scenario:

The precipitation of carbonate is primarily controlled by the availability of carbonic species. In the upper part of the depth profile, the urease breakdown produces sufficient CO_2 for the formation of carbonates, however, as indicated by the low conductivity of the soil solution, ion concentration in this realm is relatively low. Thus the amount of carbonate produced is largely controlled by the availability of suitable cations. The carbonate produced is finely dispersed throughout the sandy matrix.

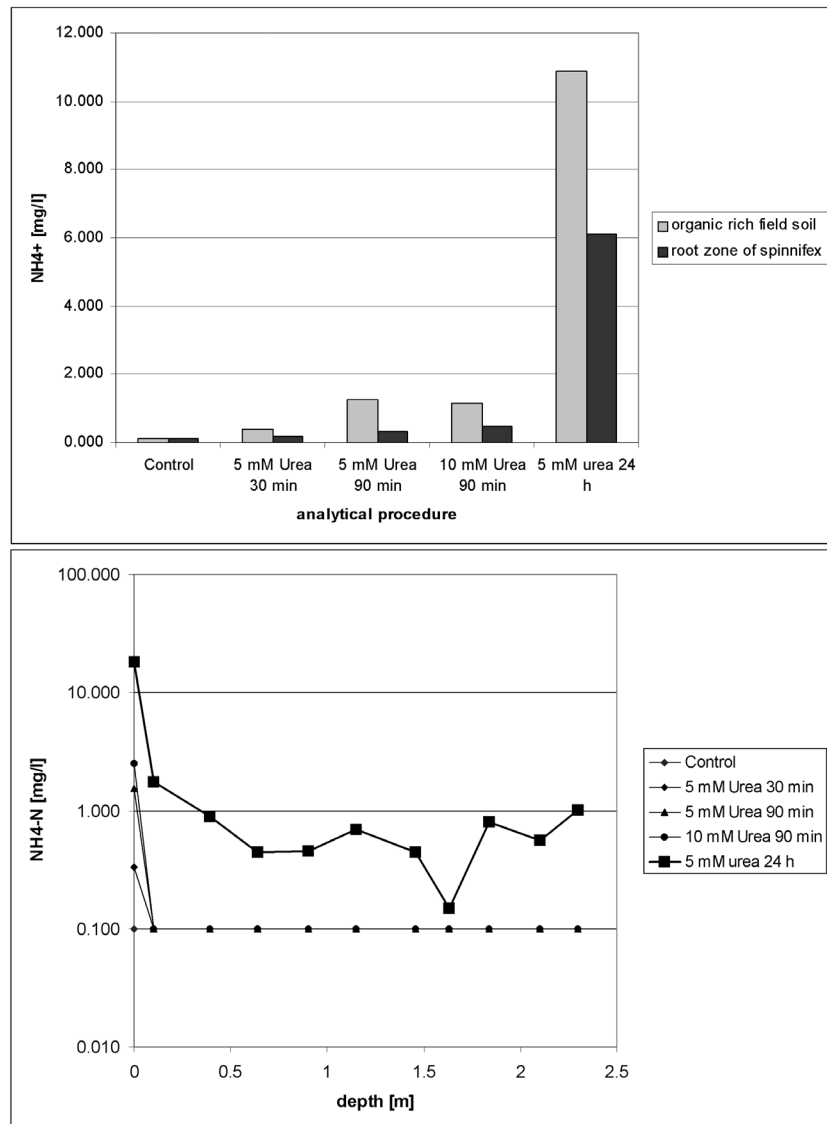


Figure 5 (top): NH_4^+ - Nitrogen production of sands after addition of urea and incubation of various times.

Figure 6 (bottom): NH_4^+ - Nitrogen production of sands from the sand dune profile after addition of urea and incubation of various times.

At depth, where ion concentration and the pH are high, carbonate could be readily precipitated. However, this is inhibited by the only sporadic influx of CO₂ saturated fluids. Thus, at depth the primary parameter controlling the formation of calcrete is the availability of carbonic species. The preferred form of carbonate precipitation is as nodular calcrete.

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